SORPTION
AND ION EXCHANGE PROCESSES

Features of the Behavior of Calcium and Magnesium Phosphate Sorbents in Water and Electrolyte Solutions

I. L. Shashkova[a], N. V. Kitikova[a], and A. I. Ivanets[a],*

[a] Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Minsk, 220072 Republic of Belarus
*e-mail: ivanets@igic.bas-net.by; andreiivanets@yandex.ru

Abstract—The hydrolytic stability of calcium and magnesium phosphates in aqueous solutions was studied in a wide pH range and in the presence of NaCl and $CaCl_2$ electrolytes: calcium hydrogen phosphate and tricalcium phosphate are stable at pH 4.5–10.0, and hydroxyapatite, at pH 3.0–12.0. An increase in the ratio of the solution volume to the weight of phosphates from 250 to 500 mL/g leads to an increase in the degree of hydrolysis by a factor of 1.4–1.9. In the presence of 0.01 M NaCl and 0.001 M $CaCl_2$, all samples exhibit high hydrolytic stability, and an increase in concentration to 1.0 M NaCl and 0.01 M $CaCl_2$ results in deprotonization of hydrophosphate ions and the transformation of magnesium phosphates to calcium phosphates.

Keywords: calcium and magnesium phosphates, sorbents, hydrolysis, hydrolytic stability, phase transformations

DOI: 10.1134/S1070427221050086

Sorption is a widely used technology for the removal of heavy metals and radionuclides due to simplicity, efficiency and low cost [1]. An important place among the sorbents used is occurred by a group of phosphate sorbents, including calcium and magnesium phosphates, which are characterized by extremely high capacity and selectivity in the adsorption of heavy metal ions and radionuclides [2–4]. The advantage of these sorbents is environmental safety, as well as the possibility of producing from natural minerals and renewable resources [5, 6].

The hydrolytic properties of calcium and magnesium phosphates must be considered when immobilizing radionuclides into phosphate matrices for safe disposal [7]. The behavior of hydroxyapatite in solution is described by various models that take into account the side processes of dissolution of the solid phase, complexation in the solution and on the surface of the solid phase, and the proceeding of phase transformations. The direction of these reactions can change significantly depending on the chemical composition of the phosphate, particle morphology, surface state [8, 9].

The hydrolytic stability of sorbents based on calcium and magnesium phosphates was practically not studied.

Previously, the relationship between the solubility of various calcium and magnesium phosphates and the sorption properties with respect to Pb^{2+}, Cr^{3+}, and Fe^{3+} ions was shown [10], as well as the possibility of phase transformations in the presence of background electrolytes in solution [11].

This work is aimed at studying the physicochemical patterns of the behavior of individual calcium and magnesium phosphates and products of phosphating of natural dolomite in aqueous solutions of various compositions.

EXPERIMENTAL

The following reagents were used as the objects of study: calcium hydrogen phosphate dihydrate $CaHPO_4 \cdot 2H_2O$, tricalcium phosphate $Ca_3(PO_4)_2$, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, magnesium ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$, as well as Ca-Mg hydrogen phosphates with the composition $Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O$ (PD-1) and Ca-Mg phosphates with an admixture of magnesium ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$ of composition $Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O$ (PD-2).

Individual phosphates were synthesized according to classical techniques [12]: sorbents PD-1 and PD-2, by phosphating of heat-treated dolomite [13]. For the synthesis of the above phosphates and for the preparation of electrolyte solutions the following reagents were used: $CaCl_2$ (reagent grade) (Reakhim JSC), $(NH_4)_2HPO_4$ (reagent grade) (Reakhim JSC), aqueous ammonia solution (25 wt %, reagent grade) (Reakhim JSC), H_3PO_4 (65 wt %, reagent grade) (Reakhim JSC), HNO_3 (65 wt %, reagent grade) (Reakhim JSC), NaCl (reagent grade) (Reakhim JSC). The pH of the working solutions was adjusted by adding 0.1 M HNO_3 solutions and a 0.1 M NaOH primary standard (Uralkhiminvest LLC).

The hydrolytic stability of these phosphates was studied:

– at the ratio of the distilled water volume (pH 5.8) to the sample weight V/m of 250 and 500 mL/g and the contact time 48 h;

– at pH of solutions in the range of 3.0–12.0 (V/m = 500 mL/g, contact time 48 h);

– in the presence of electrolytes 0.01 and 1.0 M NaCl, 0.001 and 0.01 M $CaCl_2$, prepared from the corresponding reagents at V/m = 500 mL/g and pH 6.0;

– at a variable contact time (1.0, 3.0, 5.0, 8.0, 24.0, and 48.0 h) of the PD-1 and PD-2 sorbents with solutions, at pH 3.0 and 10.0 and V/m = 500 mL/g.

A weighed portion of phosphates was poured with distilled water or an electrolyte solution, kept at room temperature with periodic stirring. After the specified time, the solution was filtered on "blue ribbon filter" paper. The precipitate was dried in air, first at room temperature, then at 65°C until constant weight. X-ray phase analysis was performed on a DRON-3 device (CuK_α radiation). The phase identification of the samples under study was carried out using the JCPDS PDF2 X-ray powder standards database.

The hydrolytic stability was assessed by the change in the pH of solutions in the course of their interaction with phosphates, by the content of PO_4^{3-}, Ca^{2+}, Mg^{2+} ions in the solution, and the total concentration of Ca^{2+} and Mg^{2+} ions. The degree of hydrolysis by phosphate ions (h_P) and by cations (h_{Cat}) was calculated using the formulas:

$$h_P = m_P/M_P \times 100\%, \qquad (1)$$
$$h_{Cat} = m_{Cat}/M_{Cat} \times 100\%, \qquad (2)$$

where m_P/M_P is the ratio of the amount of phosphate ions passed into the solution (mmol g^{-1}) to the content of phosphate ions in the sorbent (mmol g^{-1}); m_{Cat}/M_{Cat} is the ratio of the number of Ca^{2+}, Mg^{2+} or (Ca^{2+} + Mg^{2+}) cations transferred into the solution (mmol g^{-1}) to their content in the sorbent (mmol g^{-1}).

The concentration of PO_4^{3-} ions was determined by the photocolorimetric method for determining the phosphorus-molybdenum complex (maximum light absorption at a wavelength of 690 nm), formed by the interaction of phosphate ions in an acidic medium with ammonium molybdate. The concentration of Ca^{2+} and Mg^{2+} ions was found by complexometric titration at pH 10.0 in the presence of the indicator Eriochrome Black T.

RESULTS AND DISCUSSION

Hydroxyapatite, tricalcium phosphate, and calcium hydrogen phosphate significantly exceed magnesium ammonium phosphate and mixed phosphates PD-1 and PD-2 in term of hydrolytic stability in aqueous solutions (Fig. 1). Thus, the degree of hydrolysis of magnesium ammonium phosphate at V/m = 500 mL/g reaches h_{Cat} = 19.2% and h_P = 21.2%, and 22.1% and 25.7%, respectively, for sample PD-1. Under these conditions, h_{Cat} of calcium phosphates varies in the range 0.8–2.1%, h_P, in the range 2.0–4.9%. The high degree of hydrolysis of PD-1 is due to the presence of magnesium hydrophosphate in its composition [solubility product (SP) 7.6×10^{-5}], since calcium hydrogen phosphate (SP 2.7×10^{-7}) is less soluble. The hydrolysis of the PD-2 sample is due to the presence of magnesium phosphate and magnesium ammonium phosphate, which are more soluble than calcium phosphate. In terms of hydrolytic stability, the studied samples are ranked in the following order:

$$Ca_{10}(PO_4)_6(OH)_2 > CaHPO_4$$
$$\approx Ca_3(PO_4)_2 > PD\text{-}2 > MgNH_4PO_4 > PD\text{-}1. \qquad (3)$$
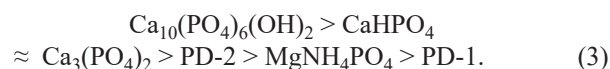
When sorbents interact with water at pH 5.8, in all cases, the concentration of phosphate ions transferred into the solution exceeds the concentration of cations. Therewith, the ratio (Ca^{2+} + Mg^{2+})/PO_4^{3-} in the initial phosphates is higher than in the solution after 48.0 h-keeping the corresponding samples. A similar behavior was noted for the samples of Ca-deficient hydroxyapatite with different molar ratios Ca^{2+}/PO_4^{3-} [14]. It was found that with a decrease in the calcium content in the initial solid phase, the solubility of
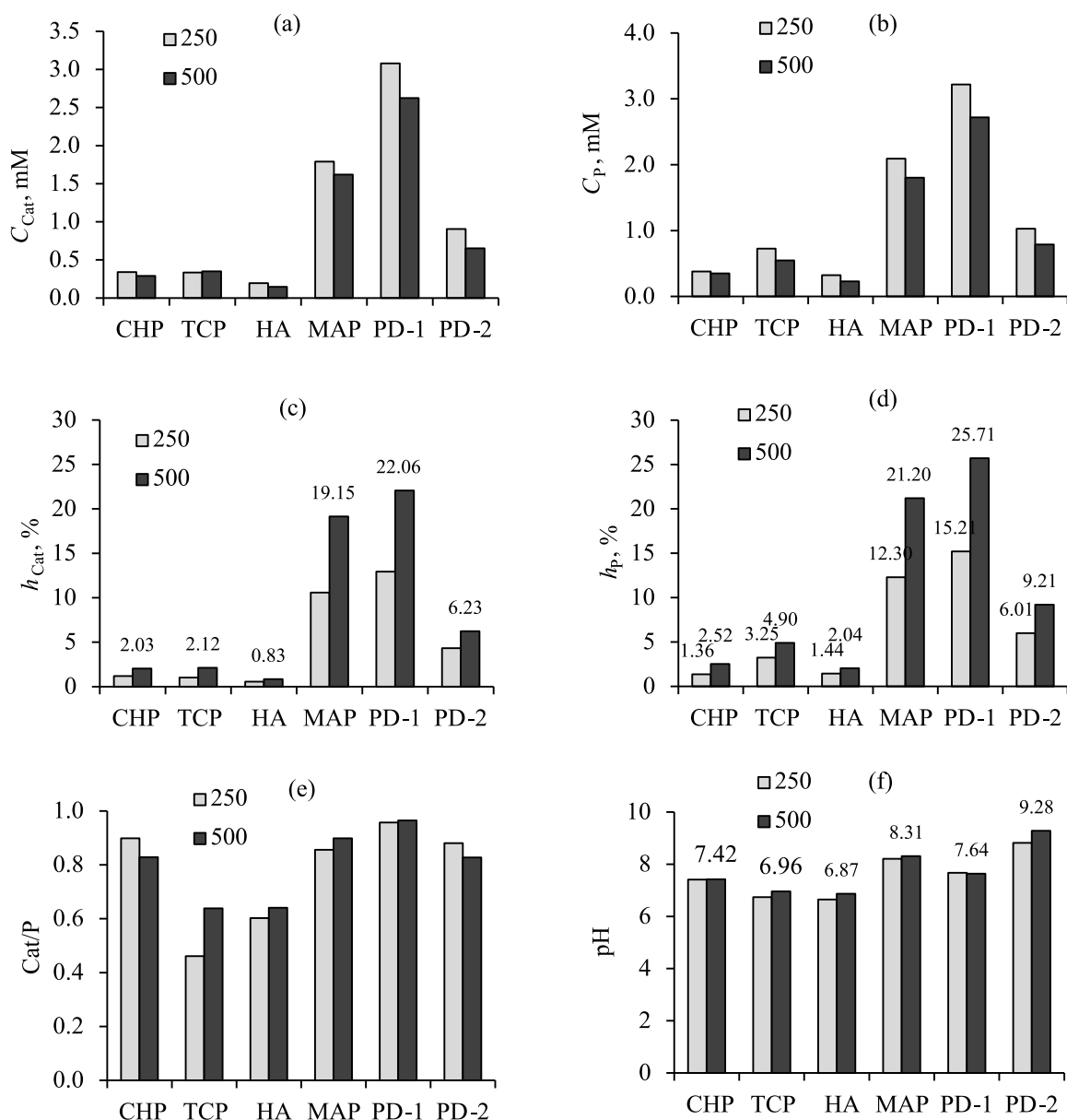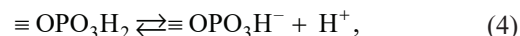
Fig. 1. (a, b) Concentrations of cations and phosphate ions in solution, (c, d) degrees of hydrolysis, (e) molar ratio of cations and phosphate ions in solution, (f) pH for phosphate samples. (CHP) $CaHPO_4 \cdot 2H_2O$, (TCP) $Ca_3(PO_4)_2$, (HA) $Ca_{10}(PO_4)_6(OH)_2$, (MAP) $MgNH_4PO_4 \cdot 6H_2O$, (PD-1) $Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O$, (PD-2) $Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O$.

hydroxyapatite in water increased, and the Ca^{2+}/PO_4^{3-} ratio decreased. This nonstoichiometric transition of ions into solution, the so-called incongruent dissolution, is characteristic of hydroxyapatite [15]. Thus, during the hydrolysis of the studied calcium and magnesium phosphates, the dissolution, complexation in the surface layer and in solution, as well as the deposition of more stable new phases occur in parallel. This fact must be taken into account when studying the mechanism of

sorption of metal ions by these phosphates.

The process of hydrolysis of the studied phosphates is accompanied by an increase in the pH of the solution (pH > 5.8) (Fig. 1f), which is due to the protonization–deprotonization and complexation on the surface of the solid phase [Eqs. (4)–(7)] and in solution [Eqs. (8)–(10)]:
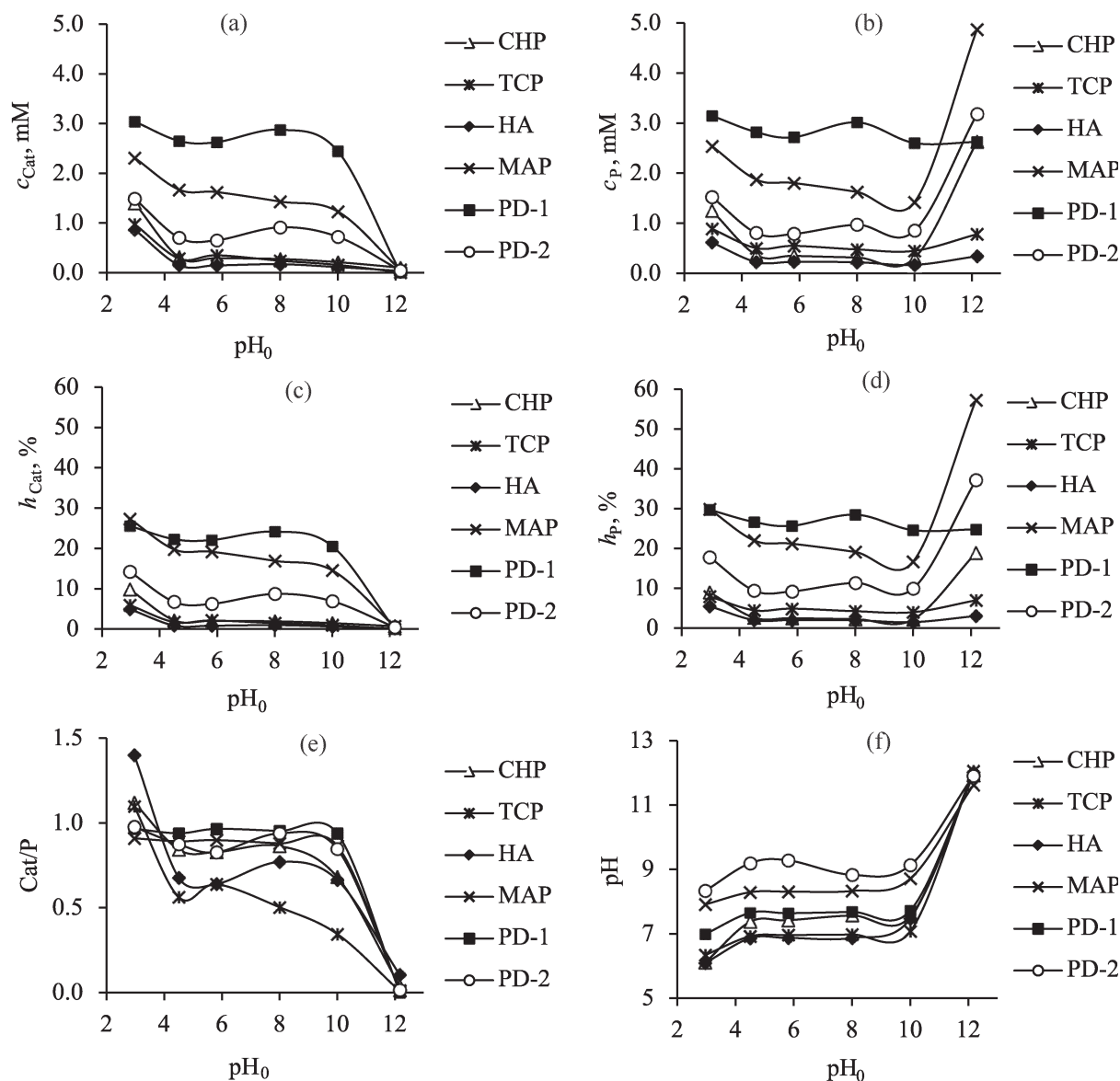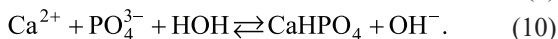
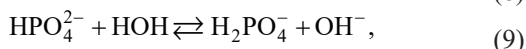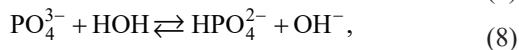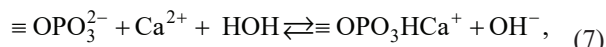$$\equiv OPO_3H_2 \rightleftarrows \equiv OPO_3H^- + H^+, \qquad (4)$$

Fig. 2. (a, b) Concentrations of cations and phosphate ions in solution and (c, d) corresponding degrees of hydrolysis, (e) molar ratio of cations and phosphate ions passed into solution, and (f) pH at different pH of the initial solutions for phosphate samples. (CHP) $CaHPO_4 \cdot 2H_2O$, (TCP) $Ca_3(PO_4)_2$, (HA) $Ca_{10}(PO_4)_6(OH)_2$, (MAP) $MgNH_4PO_4 \cdot 6H_2O$, (PD-1) $Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O$, (PD-2) $Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O$.

$$\equiv CaOH + HOH \rightleftarrows \equiv CaOH_2^+ + OH^-, \qquad (5)$$

$$\equiv CaOH_2^+ + H_2PO_4^- \rightleftarrows \equiv CaOPO_3H^- + H^+ + H_2O, \qquad (6)$$

$$\equiv OPO_3^{2-} + Ca^{2+} + HOH \rightleftarrows \equiv OPO_3HCa^+ + OH^-, \qquad (7)$$

$$PO_4^{3-} + HOH \rightleftarrows HPO_4^{2-} + OH^-, \qquad (8)$$

$$HPO_4^{2-} + HOH \rightleftarrows H_2PO_4^- + OH^-, \qquad (9)$$

$$Ca^{2+} + PO_4^{3-} + HOH \rightleftarrows CaHPO_4 + OH^-. \qquad (10)$$

A more significant change in the concentrations of cations and phosphorus in solution and the degree of hydrolysis is observed with a change in V/m for magnesium ammonium phosphate and sorbents based on phosphated dolomite, while for hydrolytically more stable calcium phosphates, the effect of V/m is insignificant (Fig. 1e). An increase in the concentration of calcium hydrogen phosphate, PD-1, and magnesium ammonium phosphate practically does not affect the pH of the solution, and for the rest of the samples it leads to a slight decrease in pH.

With an increase in the pH of the initial solution (pH_0) from 3.0 to 4.5, the degree of hydrolysis of all studied
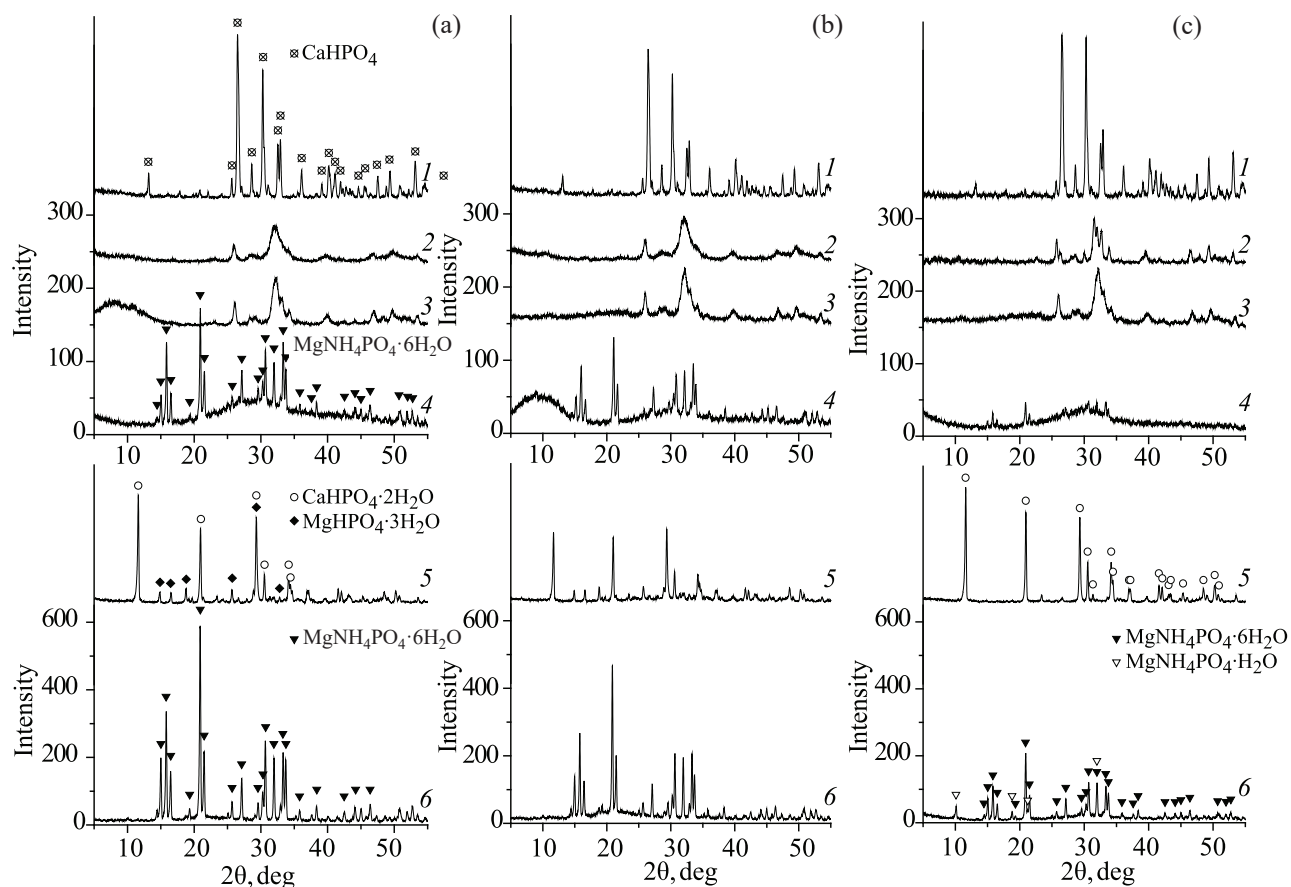
Fig. 3. X-ray patterns. (*1*) $CaHPO_4 \cdot 2H_2O$, (*2*) $Ca_3(PO_4)_2$, (*3*) $Ca_{10}(PO_4)_6(OH)_2$, (*4*) PD-2 $[Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O]$, (*5*) PD-1 $(Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O)$, and (*6*) $MgNH_4PO_4 \cdot 6H_2O$ after keeping in distilled water at (a) pH 3.0, (b) 10.0, and (c) in 0.01 M $CaCl_2$.

phosphates diminishes (Figs. 2c, 2d). As pH_0 increases from 4.5 to 10.0 for Mg-containing sorbents (magnesium ammonium phosphate, PD-1, PD-2), there is a plateau on the curves of changes in the concentrations of cations and anions and the corresponding degrees of hydrolysis. In the range of pH 10.0–12.0 for these phosphates, there is a sharp decrease in the transition of cations into the solution with a significant increase in the concentration of phosphate ions in the solution. The concentration of Ca^{2+} cations and phosphate ions in aqueous solutions during keeping calcium hydrophosphate, tricalcium phosphate, and hydroxyapatite in the pH_0 4.5–12.0 range practically does not vary and remains close to zero (Figs. 2a–2d).

The change in the molar ratio Cat/PO_4^{3-} vs. pH_0 is complex (Fig. 2e). General trends for all phosphates can be distinguished: the maximum values of Cat/PO_4^{3-} in a solution with pH_0 3.0, a plateau for most samples in the pH_0 4.5–10.0 range, and a decrease in Cat/PO_4^{3-} to zero

at pH_0 12.0. At the change in the equilibrium pH vs. pH_0 for calcium and magnesium phosphates there are three distinct regions: 3.0–4.5, 4.5–10.0, 10.0–12.0. Thus, for calcium phosphates and PD-1 in the pH_0 3.0–7.0 range and for the samples of magnesium ammonium phosphate and PD-2 in the pH_0 3.0–9.0 range, the equilibrium pH value is higher than pH_0. In the range of pH_0 9.0–12.0, the equilibrium pH values are practically equal to pH_0 for all studied phosphates (Fig. 2f).
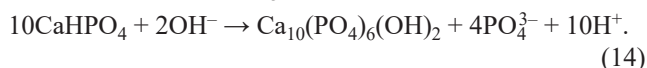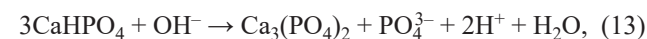
The dependence of equilibrium pH on pH_0 characterizes the state of the sorbent surface. The region of constant equilibrium pH values in the range of pH_0 4.5–10.0 corresponds to the pH of the point of zero charge (pzc) pH_{pzc} [9], which is important to take into account at sorption of metal cations from solutions. Upon pH_{pzc} increasing the studied sorbents form the following series

$$PD\text{-}2 < MgNH_4PO_4 < PD\text{-}1 \leq CaHPO_4$$
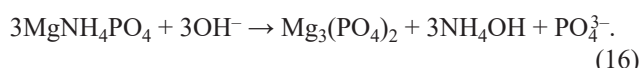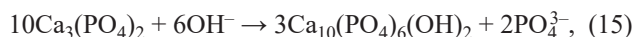$$< Ca_3(PO_4)_2 \leq Ca_{10}(PO_4)_6(OH)_2. \qquad (11)$$
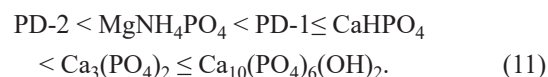
Upon contact of calcium and magnesium phosphates with water at pH_0 3.0–4.5, their phase composition does not vary (Fig. 3a). A decrease in the intensity of the main diffraction maxima of phosphate samples is observed at pH 10.0. A significant decrease in the concentration of cations in the solution for magnesium ammonium phosphate may be due to the formation of $Mg(OH)_2$ precipitate according to the scheme

$$MgNH_4PO_4 + 2OH^- \rightarrow Mg(OH)_2 + NH_4^+ + PO_4^{3-}. \quad (12)$$
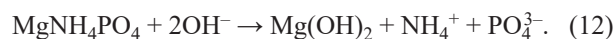
An increase in the concentration of phosphorus and the molar ratio of Ca^{2+}/PO_4^{3-} in solution at pH 12.0 as compared to the initial calcium hydrogen phosphate is due to the formation of tricalcium phosphate [Eq. (13)] and hydroxyapatite [Eq. (14)] (Fig. 3b):

$$3CaHPO_4 + OH^- \rightarrow Ca_3(PO_4)_2 + PO_4^{3-} + 2H^+ + H_2O, \quad (13)$$
$$10CaHPO_4 + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4PO_4^{3-} + 10H^+. \quad (14)$$

Tricalcium phosphate in a strongly alkaline medium (pH_0 12.0) transforms into a thermodynamically more stable phase: Ca-deficient hydroxyapatite of the composition $Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$, where $x = 0.64$ [Eq. (15)], which is proved by a decrease in the concentration of Ca^{2+} ions and a rise in the concentration of phosphate ions in solution, as well as by X-ray phase analysis data (Fig. 3b). As a result of hydrolysis of PD-2 at pH_0 10.0, a weakly crystallized $Mg_3(PO_4)_2 \cdot 22H_2O$ phase is formed according to Eq. (16):

$$10Ca_3(PO_4)_2 + 6OH^- \rightarrow 3Ca_{10}(PO_4)_6(OH)_2 + 2PO_4^{3-}, \quad (15)$$
$$3MgNH_4PO_4 + 3OH^- \rightarrow Mg_3(PO_4)_2 + 3NH_4OH + PO_4^{3-}. \quad (16)$$

In the presence of 0.01 M NaCl, the degree of hydrolysis of calcium hydrogen phosphate, tricalcium phosphate, and hydroxyapatite is less than 5%, which is close to the degree of hydrolysis in distilled water (Fig. 4a). As the NaCl concentration increases to
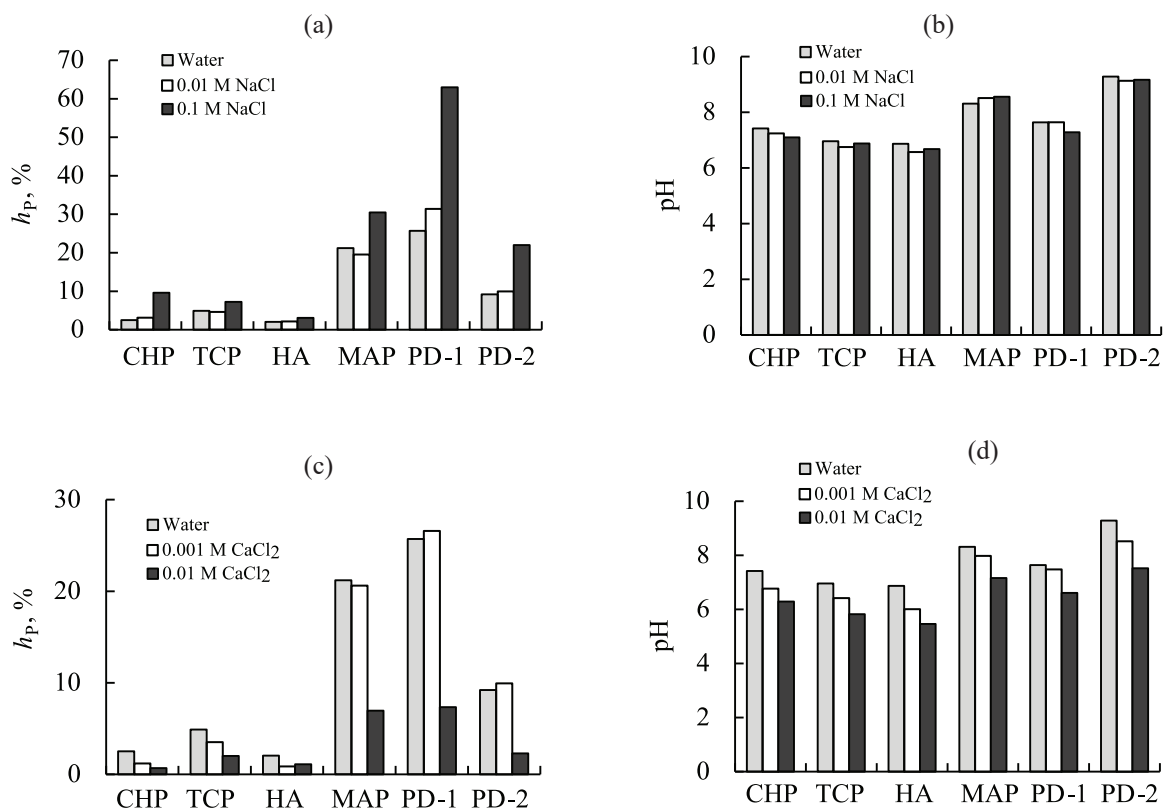

Fig. 4. (a, c) Degrees of hydrolysis with respect to phosphate ions and (b, d) pH of solutions in the presence of electrolytes (a, b) NaCl and (c, d) $CaCl_2$ for phosphate samples. (CHP) $CaHPO_4 \cdot 2H_2O$, (TCP) $Ca_3(PO_4)_2$, (HA) $Ca_{10}(PO_4)_6(OH)_2$, (MAP) $MgNH_4PO_4 \cdot 6H_2O$, (PD-1) $Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O$, (PD-2) $Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O$.
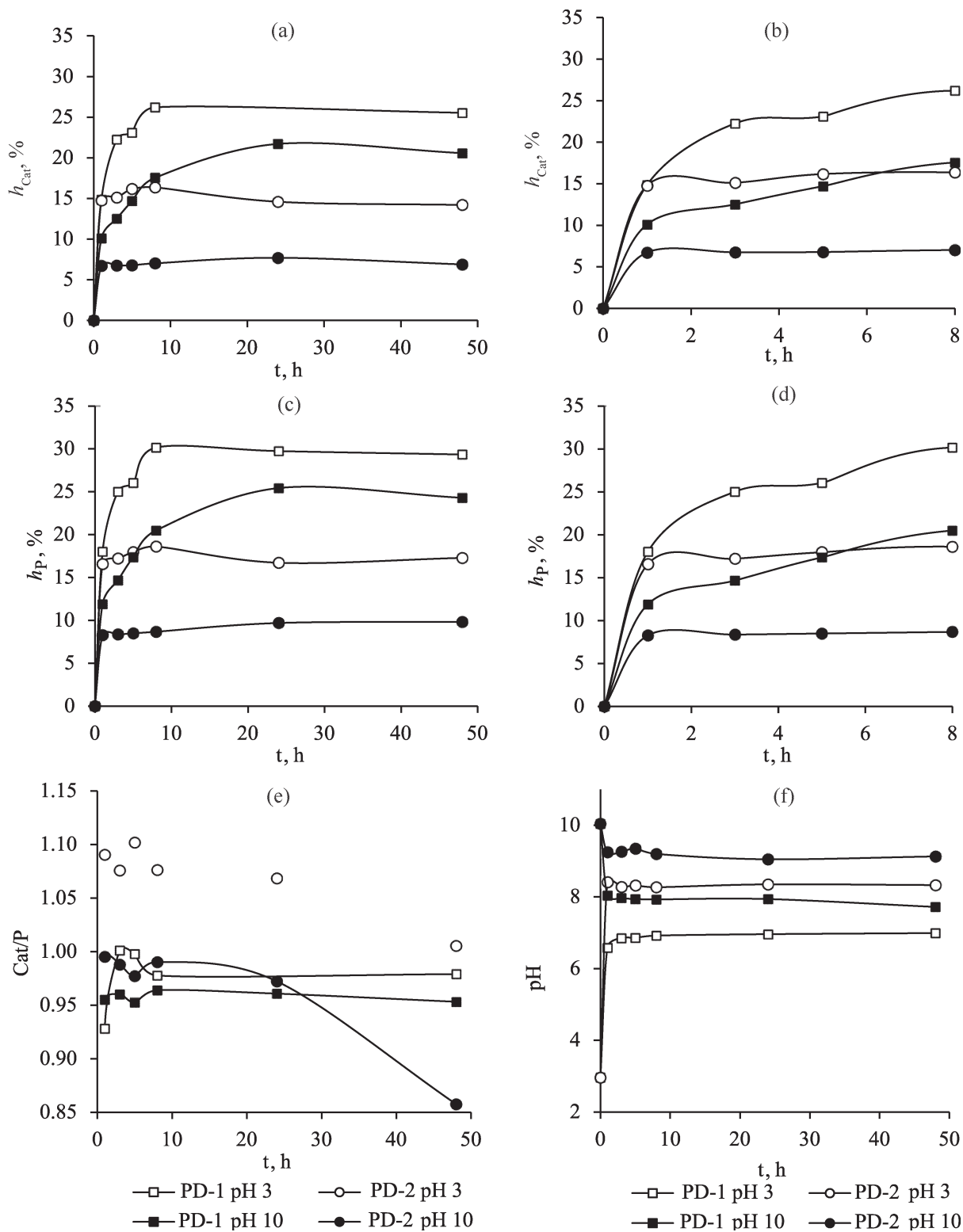
Fig. 5. (a, b) Degrees of hydrolysis with respect to cations ($Ca^{2+} + Mg^{2+}$), (c, d) phosphate ions, molar ratio (e) Cat/PO_4^{3-} in solution and (f) pH for PD-1 samples ($Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O$) and PD-2 [$Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O$].

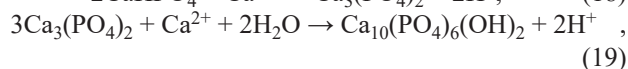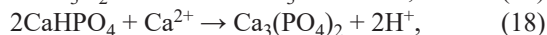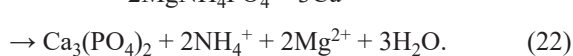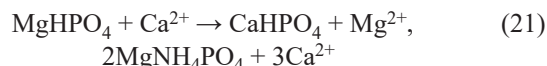1.0 M, the degree of hydrolysis of all phosphates rises 1.5–2 times, except for hydroxyapatite, the degree of hydrolysis of which in the presence of sodium cations does not change in the concentration range 0.01–1.0 M. The hydrolysis of calcium phosphates in NaCl solutions is accompanied by a slight decrease in the pH of the solutions (Fig. 4b), which can be described by Eq. (17). For Mg-containing sorbents, an inverse relationship occurs due to the peculiarities of hydrolysis, since, unlike calcium phosphates, both anions and cations undergo hydrolysis (Figs. 4a, 4b). The degree of hydrolysis of calcium and magnesium phosphates in $CaCl_2$ solutions decreases in comparison with hydrolysis in distilled water (Fig. 4c), which is accompanied by a decrease in the pH of the solution (Fig. 4d). This fact is due to a decrease in the solubility of phosphates in a $CaCl_2$ solution, the transformation of calcium hydrophosphate into tricalcium phosphate [Eq. (18)] and of tricalcium phosphate and Ca-deficient hydroxyapatite into hydroxyapatite of stoichiometric composition [(Eqs. (19), (20)]:

$$\equiv OPO_3H_2 + Na^+ \rightarrow \equiv OPO_3Na^- + 2H^+, \qquad (17)$$
$$2CaHPO_4 + Ca^{2+} \rightarrow Ca_3(PO_4)_2 + 2H^+, \qquad (18)$$
$$3Ca_3(PO_4)_2 + Ca^{2+} + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 2H^+, \qquad (19)$$

$$Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x} + xCa^{2+} + xH_2O$$
$$\rightarrow Ca_{10}(PO_4)_6(OH)_2 + 2xH^+. \qquad (20)$$
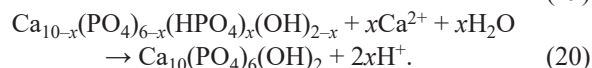
The composition of calcium hydrogen phosphate and hydroxyapatite after exposure to a $CaCl_2$ solution does not change, and tricalcium phosphate is partially converted into hydroxyapatite. PD-1 after contact with a $CaCl_2$ solution is only the $CaHPO_4 \cdot 2H_2O$ phase, with more intense reflexes of calcium hydrogen phosphate than in the original sample [Eq. (21)]. A significant decrease in the intensity of the magnesium ammonium phosphate peaks is observed for this phosphate and the corresponding impurity phase in the PD-2 sample, which also exhibits a broad reflex characteristic of tricalcium phosphate at 2θ about 30° (Fig. 3c) [Eq. (22)]:

$$MgHPO_4 + Ca^{2+} \rightarrow CaHPO_4 + Mg^{2+}, \qquad (21)$$
$$2MgNH_4PO_4 + 3Ca^{2+}$$
$$\rightarrow Ca_3(PO_4)_2 + 2NH_4^+ + 2Mg^{2+} + 3H_2O. \qquad (22)$$

The kinetics of hydrolysis was studied for samples PD-1 and PD-2, produced from natural raw materials and having the greatest practical value (Fig. 5). The hydrolysis of these phosphates proceeds at a high rate; hydrolytic equilibrium is established within 8 and 1 h for samples PD-1 and PD-2, respectively (Figs. 5a, 5b). The change in the molar ratios Cat/PO_4^{3-} (Fig. 5c) indicates the proceeding of chemical processes throughout the entire contact time of PD-1 and PD-2 with aqueous solutions at the apparent achievement of hydrolytic equilibrium (Figs. 5a–5d).

CONCLUSIONS

The studied calcium and magnesium phosphates are characterized by high hydrolytic stability in the pH range 4.5–10.0 and, in terms of hydrolytic stability, are in the following order: $Ca_{10}(PO_4)_6(OH)_2 > CaHPO_4 \approx Ca_3(PO_4)_2 >$ PD-2 $[Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O] >$ $MgNH_4PO_4 >$ PD-1 $(Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O)$. In a strongly alkaline medium at pH 12.0, calcium hydrogen phosphate is converted into tricalcium phosphate and hydroxyapatite; and tricalcium phosphate, into Ca-deficient hydroxyapatite. During the hydrolysis of these phosphates, nonstoichiometric release of cations and phosphate anion into the solution (incongruent dissolution) occurs due to the reprecipitation and complexation on the surface of the sorbents. The studied calcium and magnesium phosphates do not undergo chemical transformations in NaCl solutions. In the presence of $CaCl_2$, the composition of calcium hydrogen phosphate and hydroxyapatite does not vary, tricalcium phosphate is partially converted into hydroxyapatite, and Mg-containing phases in the samples of magnesium ammonium phosphate, PD-1 $(Ca_{0.7}Mg_{0.3}HPO_4 \cdot 2H_2O)$, and PD-2 $[Ca_{2.65}Mg_3(NH_4)_{1.3}(PO_4)_4(CO_3)_{0.3} \cdot 6H_2O]$ into calcium phosphates. The results obtained on the behavior of phosphate sorbents in aqueous solutions can be taken into account when selecting the optimal conditions for their use in purification of aqueous media from heavy metal ions and radionuclides.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Carolin, C.F., Kumar, P.S., Saravanan, A., Joshiba, G.J., and Naushad, Mu., *J. Environ. Chem. Eng.,* 2017, vol. 5, no. 3, pp. 2782–2799.

https://doi.org/10.1016/j.jece.2017.05.029

2. Singh, N.B., Nagpal, G., and Agrawal, S.R., *Environ. Technol. Innov.,* 2018, vol. 11, pp. 187–240.
https://doi.org/10.1016/j.eti.2018.05.006

3. Nzihou, A. and Sharrock, P., *Waste Biomass Valor.,* 2010, vol. 1, pp. 163–174.
https://doi.org/10.1007/s12649-009-9006-x

4. Ibrahim, M., Labaki, M., Giraudon, J.-M., and Lamonier, J.-F., *J. Hazard. Mater.,* 2019, vol. 383, p. 121139.
https://doi.org/10.1016/j.jhazmat.2019.121139

5. Imam, D.M., Moussa, S.I., and Attallah, M.F., *J. Radioanal. Nucl. Chem.,* 2019, vol. 319, pp. 997–1012.
https://doi.org/10.1007/s10967-018-06403-7

6. Smičiklas, I., Onjia, A., Raičevic, S., Janackovic, D., and Mitrić, M., *J. Hazard. Mater.,* 2008, vol. 152, pp. 876–884.
https://doi.org/10.1016/j.jhazmat.2008.06.044

7. Vinokurov, S.E., Kulikova, S.A., Myasoedov, B.F., *J. Radioanal. Nucl. Chem.,* 2018, vol. 318, no. 3, pp. 2401–2405.
https://doi.org/10.1007/s10967-018-6181-x

8. Bengtsson, Å., Shchukarev, A., and Persson, P., Sjöberg, S., *Geochim. Cosmochim. Acta,* 2009, vol. 73, no. 2, pp. 257–267.
https://doi.org/10.1016/j.gca.2008.09.034

9. Kwon, K.-Y., Wang, E., Chung, A., Chang, N., and Lee, S.-W., *J. Phys. Chem.,* pp. 2009, vol. 113, no. 9, pp. 3369–3372.
https://doi.org/10.1021/jp810414z

10. Shashkova, I.L., Ratʹko, A.I., and Kitikova, N.V., *Colloid Surf. A,* 1999, vol. 160, no. 3, pp. 207–215.
https://doi.org/10.1016/S0927-7757(99)00193-4

11. Ivanets, A.I., Kitikova, N.V., Shashkova, I.L., Kulʹbitskaya, L.V., *Russ. J. Appl. Chem.,* 2015, vol. 88, no. 2, pp. 232–238.
https://doi.org/10.1134/S107042721502007X

12. Shchegrov, L.N., *Fosfaty dvukhvalentnykh metallov* (Divalent Metal Phosphates), Kiev: Naukova Dumka, 1987.

13. Ivanets, A.I., Kitikova, N.V., Shashkova, I.L., Oleksiienko, O.V., Levchuk, I., and Sillanpää, M., *J. Water Proc. Eng.,* 2016, vol. 9, pp. 246–253.
https://doi.org/10.1016/j.jwpe.2016.01.005

14. Mavropoulos, E., Rossi, A.M., da Rocha, N.C.C., Soares, G.A., Moreira, J.C., and Moure, G.T., *Mater. Charact.,* 2003, vol. 50. N 2–3, pp. 203–207.
https://doi.org/10.1016/S1044-5803(03)00093-7

15. Dorozhkin, S.V., *World Methodol.,* 2012, vol. 2, no. 1, pp. 1–17.
https://doi.org/10.5662/wjm.v2.i1.1